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(54) SILICA BASED FINE PARTICLE AND ITS MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide silica based fine particles having projections which have strongly been integrated by chemical bonding over the entire surface of matrix particles and suitable, e.g., as the filler for resins and the matrix of conductive particles coated with a conductive layer in its surface, and a method for manufacturing the same.

SOLUTION: The silica based fine particles have substantially spherical and/or hemispherical projections over the entire surface of matrix particles, the projections being integrated with the matrix particles by chemical bonding. The method for manufacturing the silica based fine particles comprises (A) a step of hydrolyzing and condensing a specific alkoxysilane compound to form polyorganosiloxane particles, (B) a step of surface-treating the polyorganosiloxane particles with a surface adsorbent, and (C) a step of forming projections over the entire surface of the polyorganosiloxane particles having been surface-treated in the above step (B) with the use of the above alkoxysilane compound.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to a silica system particle and its manufacture approach. This invention relates to a silica system particle suitable as a base material of the conductive particle which the projection of the shape of a ball or a semi-sphere bound to the whole parent particle surface firmly by the chemical bond mostly, for example, covered the conductive layer on the filler for resin, or the front face etc., and the method of manufacturing this thing efficiently in more detail.

[0002]

[Description of the Prior Art] Conventionally, in semi-conductor resin encapsulant, a radial-ply tire, etc., it is the purpose which raises the engine performance and various fillers are mixed. As this filler, an inorganic system particle and glass fiber are mainly used. When it is the case where a filler is a spherical particle, and a konpeito-like particle and these are used as fillers, such as semi-conductor resin encapsulant and a radial-ply tire, latter one is excellent in respect of adhesion with a resin constituent or a rubber constituent, or the prevention effectiveness of the crack initiation resulting from a coefficient-of-thermal-expansion difference.

[0003] About manufacture of a konpeito-like particle, conventionally, for example under existence of the distributed polymerization particle obtained by (1) distribution polymerization method The resin particle which has irregularity on the front face which makes a minute polymer particle come to adhere to the front face of this distributed polymerization particle by carrying out the polymerization of the monomer (JP,5-331216,A), (2) Use adhesives for the front face of a mother particle, and make a child particle adhere to it, or welding is carried out directly. By evaporating a solvent, putting into the approach of producing the particle which has a projection in a front face, or the container turning around a mother particle, making the solution of a child particle adhere to this particle front face, and rotating a container The approach (JP,4-36902,A) and (3) melting spherical silica particle which produce the particle which a solute is deposited in corniform and has a projection in a mother particle front face, Injection processing of the letter silica particle of crushing more detailed than this silica particle is carried out into a high-speed rotation air current, and the approach (JP,3-259960,A) of producing the particle which has a projection on a particle front face etc. is indicated.

[0004] However, since the parent particle and the projection have joined by physical adhesion and welding, the particle which the resin particle which has irregularity on the surface of the above (1) has the fault of being scarce, in the particle itself, or the shear strength and disruptive strength of a projection, and has a projection on the other hand on the front face obtained by the approach of (2) and (3) has the fault of being scarce, in the shear strength and disruptive strength of a projection. Moreover, in the approach of the above (3), since processing is performed under a high-speed rotation air current, there are also problems, like the thermal resistance and pressure resistance of the particle itself are needed. When such a konpeito-like particle is used as a filler, a difference arises in mechanical strengths, such as disruptive strength of the product itself obtained, according to the difference of the

bond strength of a parent particle front face and a projection.

[0005]

[Problem(s) to be Solved by the Invention] This invention is the basis of such a situation, and it goes over it all over a parent particle, and it aims at offering a silica system particle suitable as a base material of the conductive particle which the projection came to bind by the chemical bond firmly, for example, covered the conductive layer on the filler for resin, or the front face etc.

[0006]

[Means for Solving the Problem] The process which the alkoxysilane compound of specific structure is hydrolyzed [process] and makes a polyorganosiloxane particle generate as a result of repeating research wholeheartedly, in order that this invention persons may attain said purpose, The process which carries out surface treatment of this polyorganosiloxane particle, and this surface treatment polyorganosiloxane particle are made into a seed particle. This process in which use an alkoxysilane compound for all over a particle, and a projection is made to form, and by giving baking down stream processing by the case further Based on a header and this knowledge, it came to complete this invention for the silica system particle which the projection of the shape of the shape of a parenchyma top ball or a semi-sphere comes to bind to the whole parent particle surface by the chemical bond firmly being obtained.

[0007] That is, all over a parent particle, on parenchyma, it is the silica system particle which has a semi-sphere-like projection, and this inventions are spherical and/or a thing which offers the silica system particle characterized by this projection binding to the parent particle by the chemical bond.

[0008] Moreover, the above-mentioned silica system particle is the (A) general formula (I).

$R_1nSi(OR_2)_{4-n} \dots (I)$

the inside of a formula, and R_1 -- the alkyl group of carbon numbers 1-5, and the alkenyl radical of carbon numbers 2-5 -- the aryl group of carbon numbers 6-10 or the aralkyl radical of carbon numbers 7-10, and R_2 show the alkyl group of carbon numbers 1-5, and n shows 1 or 2, when n is 2, even if two R_1 is mutually the same, you may differ, and even if two or more OR_2 is mutually the same, it may differ. The process which the alkoxysilane compound expressed is made as hydrolysis, and carries out particle-size growth and makes a polyorganosiloxane particle to carry out condensation and generate by making into a seed particle the particle obtained by the case, (B) The process which carries out surface treatment of the polyorganosiloxane particle obtained at the above-mentioned (A) process with a surface adsorbent, And the polyorganosiloxane particle by which surface treatment was carried out at the (C) above-mentioned (B) process is made into a seed particle. It can manufacture using the alkoxysilane compound expressed with said general formula (I) by this process in which a projection is made to form all over a seed particle, and the approach of containing (D) baking down stream processing by the case further.

[0009]

[Embodiment of the Invention] It goes over the silica system particle of this invention all over a parent particle, and they are spherical and/or a konpeito-like particle which a semi-sphere-like projection comes to bind by the chemical bond firmly on parenchyma. It sets to a silica system particle and both a projection and a parent particle are usually a general formula (I).

$R_1nSi(OR_2)_{4-n} \dots (I)$

It has the presentation which comes out and originates in the alkoxysilane compound expressed. In this case, the alkoxysilane compound of the raw material which forms a projection, and the alkoxysilane compound of the raw material which forms a parent particle may be the same, and may differ from each other.

[0010] In said general formula (I), R_1 shows the alkyl group of carbon numbers 1-5, the alkenyl radical of carbon numbers 2-5, the aryl group of carbon numbers 6-10, or the aralkyl radical of carbon numbers 7-10. Here, the alkyl groups of carbon numbers 1-5 may be any of the shape of a straight chain, and the letter of branching, and a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, tert-butyl, and various pentyl radicals are mentioned as the example. The alkenyl radicals of carbon numbers 2-5 may be any of the shape of a straight chain, and the letter of

branching, and a vinyl group, an allyl group, a butenyl group, a pentenyl radical, etc. are mentioned as the example. As an example of the aryl group of carbon numbers 6-10, a phenyl group, a tolyl group, a xylyl group, a naphthyl group, etc. are mentioned, and benzyl, a phenethyl radical, a phenylpropyl radical, a naphthyl methyl group, etc. are mentioned as an example of the aralkyl radical of carbon numbers 7-10.

[0011] On the other hand, R2 is the alkyl group of carbon numbers 1-5, this alkyl group may be any of the shape of a straight chain, and the letter of branching, and a methyl group, an ethyl group, n-propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, tert-butyl, and various pentyl radicals are mentioned as that example. n is 1 or 2, and when n is 2, even if two R1 is mutually the same, you may differ, and even if two or more OR2 is mutually the same, it may differ.

[0012] As an example of an alkoxysilane compound expressed with said general formula (I), methyl trimethoxysilane, methyl triethoxysilane, a methyl tripropoxy silane, a methyl triisopropoxy silane, ethyltrimethoxysilane, ethyltriethoxysilane, propyl triethoxysilane, butyltrimethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, dimethyldimethoxysilane, methylphenyl dimethoxysilane, etc. are mentioned. In these, especially methyl trimethoxysilane and vinyltrimethoxysilane are suitable.

[0013] In this invention, one sort of alkoxysilane compounds expressed with said general formula (I) may be used as a raw material, and you may use combining two or more sorts. 0.5-30 micrometers of mean particle diameter are usually 2-10 micrometers preferably, and the coefficient of variation (CV value) of particle size distribution is usually 5% or less, and the parent particle in the silica system particle of this invention is a real ball-like monodisperse particle.

[0014] In addition, coefficient of variation (CV value) is called for by the bottom type.

CV value (%) = (standard deviation/mean particle diameter of particle size) x 100 -- the projection currently bound to the whole surface of this parent particle by the chemical bond has the configuration of the shape of spherical and/or a semi-sphere on parenchyma, and the range of the average of the height / parent particle diameter of a projection is usually 0.02-0.5. Moreover, the number of the projections currently bound to one parent particle is influenced by the value of the height / parent particle diameter of the above-mentioned projection, and is not limited especially.

[0015] Furthermore, as for the silica system particle of this invention, about what was silica-ized completely, nitrogen adsorption specific surface area becomes large more than twice [about] compared with the conventional spherical silica system particle (it does not have a projection) with the same particle diameter. The silica system particle of this invention which has such a configuration can be efficiently manufactured by the approach of this invention shown below.

[0016] The manufacture approach of the silica system particle of this invention explains [next] each process including the generation process of (A) polyorganosiloxane particle, the surface treatment process of (B) this polyorganosiloxane particle, (C) projection formation process, and (D) baking down stream processing given by the case.

[0017] (A) It is the process which the alkoxysilane compound by which ***** of a polyorganosiloxane particle is expressed with said general formula (I) is made as hydrolysis in this (A) process, and carries out particle-size growth and makes a polyorganosiloxane particle to carry out condensation and generate by making into a seed particle the particle obtained by the case.

[0018] In this (A) process, although the alkoxysilane compound expressed with said general formula (I) under existence of the ammonia which contains a nonionic surfactant by request, and/or the aqueous solution of an amine is carried out hydrolysis and condensation, the above-mentioned ammonia and an amine are the catalysts of the hydrolysis and the condensation reaction of this alkoxysilane compound. Here, as an amine, monomethylamine, dimethylamine, a monoethyl amine, diethylamine, ethylenediamine, etc. can be mentioned preferably, for example. Although this ammonia and amine may be used independently and you may use combining two or more sorts, there is little toxicity, removal is easy, and since it is cheap, ammonia is suitable.

[0019] As the ammonia containing a nonionic surfactant, and/or an aqueous solution of an amine, the solution which dissolved a nonionic surfactant, ammonia, and/or an amine in the partially aromatic

solvent of water or water, and a water miscibility organic solvent is mentioned. Here, as an example of a water miscibility organic solvent, ether, such as ketones, such as lower alcohol, such as a methanol, ethanol, propanol, and a butanol, an acetone, dimethyl ketone, and a methyl ethyl ketone, diethylether, and dipropyl ether, etc. is mentioned. These may be independently mixed with water and may be mixed with water combining two or more sorts. Although there is especially no limit as amount of ammonia or the amine used, it is desirable to select so that pH of the water layer before reaction initiation may become the range of 7.5-11.0.

[0020] In this invention, what has an HLB value in the range of 8-20 is preferably used as a nonionic surfactant used by request. This HLB is an index showing a hydrophilic property and oleophilic balance, and oleophilic is so high that that value is small. In that by which an HLB value deviates from the above-mentioned range, the effectiveness of this invention is not fully demonstrated. In order to more often demonstrate the effectiveness of this invention, what has an HLB value in the range of 10-17 is desirable.

[0021] Although there is especially no limit as a reaction format and both mixed homogeneous reaction and a two-layer system reaction can be used, a CV value is small, a particle with a sufficient particle-size precision is obtained, and a point with easy reaction actuation to the two-layer system reaction is more advantageous.

[0022] In this two-layer system reaction, that whose specific gravity (23 degrees C) of the independent object expressed with said general formula (I) or mixture is one or less as an alkoxysilane compound of a raw material is used. First, it is made to react by the interface, holding a two-layer condition without mixing this alkoxysilane compound with the nonionic surfactant, the ammonia, and/or the amine content aqueous solution which are used by request on parenchyma.

[0023] In this reaction, it is required to agitate gently so that a two-layer condition may be held, without mixing an alkoxysilane compound, and ammonia and an amine aqueous solution layer on parenchyma. By this, the upper alkoxysilane compound is hydrolyzed, it shifts to a lower layer, and a polyorganosiloxane particle grows there. Although the reaction temperature in this case is influenced by the class of alkoxysilane compound of a raw material etc., generally it is chosen in 0-60 degrees C. In this two-layer system reaction, after the upper alkoxysilane compound disappears, degree process is supplied.

[0024] In the (A) process of this invention, if needed, the particle obtained by doing in this way may be made into a seed particle, and may carry out particle-size growth further. In this case, after making a seed particle generate, a dilution scale factor is desirable, reaction mixture is diluted with an aqueous medium so that it may increase 5 to 100 times more preferably two to 200 times, and seed particle liquid is prepared. Under the present circumstances, as an aqueous medium used for dilution, although the partially aromatic solvent of water or water, and a water miscibility organic solvent is used, it is desirable to use the same thing as what was used as a reaction medium in said hydrolysis reaction.

[0025] Next, the alkoxysilane compound expressed with said general formula (I) is added in this seed particle liquid, a two-layer system reaction is performed in it like the above, and a seed particle is grown up into it. This actuation can be repeatedly performed until it makes it grow up to be a desired particle size.

[0026] (B) It is the process which carries out surface treatment of the polyorganosiloxane particle from which the surface place science and engineering of a polyorganosiloxane particle was obtained at the aforementioned (A) process in this (B) process with a surface adsorbent.

[0027] Under the present circumstances, as a surface adsorbent to be used, polyvinyl alcohol, a polyvinyl pyrrolidone, and a surfactant can be mentioned preferably, for example. as polyvinyl alcohol - whenever [saponification] -- desirable -- 34-98-mol % -- it is 88-98-mol % more preferably, and 200-3,500, and the thing that is in the range of 500-2,400 more preferably are [number average molecular weight is desirable and] suitable. Moreover, as a polyvinyl pyrrolidone, number average molecular weight is desirable and 10,000-360,000, and the thing that is in the range of 40,000-120,000 more preferably are suitable.

[0028] On the other hand, as a surfactant, a nonionic and anionic thing is used preferably. As a nonionic

surfactant, what has an HLB value in the range of 8-20 is used preferably. This HLB is an index showing a hydrophilic property and oleophilic balance, and oleophilic is so high that that value is small. In that by which an HLB value deviates from the above-mentioned range, the effectiveness of this invention is not fully demonstrated. In order to more often demonstrate the effectiveness of this invention, what has an HLB value in the range of 10-17 is desirable.

[0029] That what is necessary is just what has an HLB value in the above-mentioned range as this nonionic surfactant. It is not restricted especially. For example, polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, The polyoxyethylene sterol ether, a polyoxyethylene lanolin derivative, The ethylene oxide derivative of an alkylphenol formalin condensate, a polyoxyethylene polyoxypropylene blockpolymer, Ether mold nonionic surfactants, such as polyoxyethylene polyoxypropylene alkyl ether, Polyoxyethylene glycerine fatty acid ester, polyoxyethylene castor oil, and hydrogenated castor oil, Ether ester mold nonionic surfactants, such as polyoxyethylene sorbitan fatty acid ester and polyoxyethylene sorbitol fatty acid ester, Polyethylene glycol fatty acid ester, polyglyceryl fatty acid ester, A sorbitan fatty acid ester, propylene glycol fatty acid ester, Although nitrogen-containing mold nonionic surface active agents, such as ester mold nonionic surface active agents, such as sucrose fatty acid ester, polyoxyethylene fatty acid amide, polyoxyethylene alkylamine, and alkylamine oxide, etc. are mentioned. An ether mold is desirable in these and especially polyoxyethylene alkyl phenyl ether is suitable. These nonionic surfactants may be used independently and may be used combining two or more sorts.

[0030] Moreover, as an anionic surfactant, what has an HLB value in the range of 18-42 is used. In that by which an HLB value deviates from the above-mentioned range, the effectiveness of this invention is not fully demonstrated. As such an anionic surfactant, that an HLB value should just be in the range of 18-42, although there is especially no limit, alkylaryl sulfonates, alkyl sulfate, fatty-acid alkali salt, alkyl phosphate, alkyl phosphonate, etc. are mentioned, for example. In these, the carbon number of an alkyl group has [the alkylaryl sulfonates of 8-18, and the carbon number of an alkyl group / the alkyl sulfate of 8-18, and the carbon number of an alkyl group] the desirable fatty-acid alkali salt of 8-18, and sodium dodecyl sulfate, dodecylbenzene sulfonate, and an oleic acid potassium are especially suitable. Moreover, this anionic surfactant may be used independently and may be used combining two or more sorts.

[0031] In this (B) process, after carrying out churning mixing of the polyorganosiloxane particle liquid obtained at the aforementioned (A) process, and the aqueous solution containing the above-mentioned surface adsorbent, surface treatment is performed by adding ammonia and/or an amine and riping in the temperature of 20-60 degrees C for about 1 to 20 hours preferably. Under the present circumstances, the concentration of the surface adsorbent in the above-mentioned mixed liquor has 0.1 - 5% of the weight of the desirable range. Thus, preferably, after isolating the polyorganosiloxane particle by which surface treatment was carried out, it is supplied to the projection formation process of degree process.

[0032] (C) They are hydrolysis and the process in which carry out condensation and a projection is made to form all over this seed particle (parent particle) about the alkoxysilane compound by which projection ***** makes a seed particle the polyorganosiloxane particle by which surface treatment was carried out at the aforementioned (B) process, and is expressed with said general formula (I) in this (C) process. Also in this (C) process, although both mixed homogeneous reaction and a two-layer system reaction can be used, the two-layer system reaction is more advantageous like the aforementioned (A) process.

[0033] In this two-layer system reaction, the aqueous liquid which makes it come to distribute the surface treatment polyorganosiloxane particle obtained at the aforementioned (B) process in the aqueous solution which contains first the dispersant, the ammonia, and/or the amines which are used by request, such as polyvinyl alcohol, is prepared. Subsequently, it is made to react by the interface, without mixing with this aqueous liquid on parenchyma the alkoxysilane compound expressed with a general formula (I), holding a two-layer condition.

[0034] In this reaction, it is required to agitate gently so that a two-layer condition may be held, without mixing an alkoxysilane compound, and ammonia and an amine aqueous solution layer on parenchyma. By this, the upper alkoxysilane compound is hydrolyzed, it shifts to a lower layer, a chemical bond is

carried out to the polyorganosiloxane particle of a parent particle there, and a projection is grown up. Although the reaction temperature in this case is influenced by the class of alkoxysilane compound of a raw material etc., generally it is chosen in 0-60 degrees C.

[0035] After centrifugal separation and a sedimentation classification perform particle washing according to a conventional method, spherical and/or the silica system particle which has a semi-sphere-like projection are obtained on parenchyma all over a parent particle by carrying out desiccation processing after reaction termination (after the upper layer's disappearing). In this invention, since the silica system particle obtained by doing in this way consists of polyorganosiloxanes in which a parent particle and a projection have an organic radical, it can perform the next baking processing if needed.

[0036] (D) Set baking place science and engineering at this (D) process. It responds to the application of a final product. Baking processing Under existence of oxygen content gas, such as air, Preferably, 500-1000 degrees C, may carry out at the temperature of the range of 600-900 degrees C more preferably, may perform perfect silica-ization, may obtain the rate particle of high elasticity, and Or 400-900 degrees C of baking processings may be more preferably performed at the temperature of the range of 500-800 degrees C the bottom of inert gas ambient atmospheres, such as nitrogen, or into a vacuum, formation of a partial silica or non-silica-ization may be performed, and a low elastic-modulus particle may be obtained. Namely, what is necessary is just to select the optimal conditions according to needed disruptive strength and elastic modulus. Moreover, although there is especially no limit about baking equipment and an electric furnace, rotary kiln, etc. can be used, calcinating in the rotary kiln which can agitate a particle is advantageous. Thus, the configurations of the particle which comes to carry out baking processing are a baking front and similarity on parenchyma, and it goes over them all over a parent particle, and they have the shape of konpeito which the projection of the shape of the shape of a ball or a semi-sphere bound firmly by the chemical bond mostly.

[0037]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

[0038] The glass flask of 500ml ** was set to the constant temperature bath with a magnetic stirrer in which the preparation temperature control of the example 1(1) 1st seed particle liquid is possible, the liquid which mixed the polyoxyethylene-alkyl-aryl-ether "noy gene EA-137 (HLB13)" [product made from first Heavy chemicals] 0.3 ml and 300g of ion exchange water which is 12ml of aqueous ammonia of one-mol [1.] concentration and the Nonion system surface active agent was put in, and temperature was held at 30 degrees C at this. Subsequently, after it poured in methyl trimetoxysilane (MTMS) 30g on this liquid so that an interface might not be confused, and considering as the two-layer condition, the lower layer aqueous ammonia solution was gently agitated with the magnetic stirrer, and the hydrolysis reaction of MTMS was performed. With the passage of time, a lower layer aqueous ammonia solution began to become cloudy, and 3 hours after, the upper MTMS shifted into the lower layer aqueous ammonia solution by hydrolysis, and disappeared. Into this nebula liquid, the mono dispersion poly methyl silsesquioxane (PMSO) particle of 1.85 micrometers of mean diameters was generating, and this was made into the 1st seed particle liquid.

[0039] (2) Setting the 5l. glass flask equipped with the preparation churning motor and impeller of the 2nd seed particle liquid to a constant temperature bath, putting 4500ml of ion exchange water into this flask, and agitating by 20rpm, the whole quantity of the 1st seed particle liquid obtained above (1) is added, and the seed PMSO particle was diluted and it was made to distribute. Subsequently, the hydrolysis reaction was again performed in the state of two-layer, having filled the upper layer of these dispersion liquid with MTMS450g, and having used reaction temperature as 30 degrees C, and growth reaction of a seed PMSO particle was performed. 5 hours after, when the upper MTMS disappeared, the PMSO particle was growing to 5.0-5.2 micrometers with mean particle diameter, and was a mono dispersion spherical particle. This was made into the 2nd seed particle liquid.

[0040] (3) To the 2nd seed particle liquid whole quantity of surface preparation, 1200ml (PVA water solution) of polyvinyl alcohol [full saponification mold and number average molecular weight (Mn) 500] water solutions of concentration was added 5% of the weight, churning mixing was carried out, and

the seed PMSO particle dispersion liquid whose PVA concentration is 1 % of the weight were prepared. Subsequently, after adding 15ml of aqueous ammonia 25% of the weight, the temperature up of the solution temperature was carried out to 50 degrees C, and it held at the temperature for 12 hours. The PVA adsorption PMSO particle (parent particle) obtained here was a mono dispersion particle with a mean particle diameter of 4.5 micrometers. Next, this was dried after washing with the methanol and 190g of seed fine particles was obtained.

[0041] (4) The 1l. glass flask was set to the constant temperature bath with a magnetic stirrer in which anomaly-ized processing temperature control is possible, the liquid which made 800ml of PVA water solutions distribute 2g of seed fine particles obtained above (3) to this 1% of the weight, and the liquid which mixed 0.1ml of aqueous ammonia 25% of the weight were put in, and temperature was held at 30 degrees C. Subsequently, after it poured in methyl trimetoxysilane (MTMS) 70g on this liquid so that an interface might not be confused, and considering as the two-layer condition, the lower layer aqueous ammonia solution was gently agitated with the magnetic stirrer, and the hydrolysis reaction of MTMS was performed. With the passage of time, a lower layer aqueous ammonia solution began to become cloudy, and 2 hours after, the upper MTMS shifted into the lower layer aqueous ammonia solution by hydrolysis, and disappeared.

[0042] As a result of taking out a particle and observing a configuration with a scanning electron microscope (SEM), it had the projection with a height of 1.4-3.0 micrometers all over the particle, and was the particle of the shape of konpeito whose apparent mean particle diameter [the particle size (the following last mean particle diameter and notation) included to the projection tip] is 6.5 micrometers. The SEM photograph Fig. of this particle is shown in drawing 1. Next, after performing particle washing and distributing a methanol finally by centrifugal separation and the sedimentation classification, removed the methanol, it was made to dry in 120-degree C oven, and 1.8g of desiccation particles was obtained.

[0043] (5) A temperature up is carried out to 800 more degrees C in 0.5 hours, and after holding at the temperature for 6 hours, the temperature was made to lower to a room temperature, after putting the desiccation particle obtained by the baking processing above (4) into a baking container, setting it into an electric furnace, carrying out the temperature up of the air from a room temperature to 400 degrees C with a sink by 0.3l. the flow rate for /in 1.25 hours and holding at the temperature for 48 hours. The configurations of a particle were a baking front and similarity. As a result of IR measurement, the peak of a methyl group was not observed, but IR absorption of only a silica was accepted, and changing to the silica was checked. In addition, the low elastic-modulus variant particle to which neither has silica-ized it by the 0.3l. flow rate for /when nitrogen is calcinated at 2.5 hours or 670 degrees C by 690 degrees C with a sink for 2.5 hours was obtained in the desiccation particle.

[0044] The same actuation as (1) - (3) in example 2 example 1 was performed, and seed fine particles were obtained.

(1) The 1l. glass flask was set to the constant temperature bath with a magnetic stirrer in which anomaly-ized processing temperature control is possible, the liquid which made this distribute the 2g of the above-mentioned seed fine particles in 800ml of PVA water solutions 1% of the weight, and the liquid which mixed 0.1ml of aqueous ammonia 25% of the weight were put in, and temperature was held at 30 degrees C. Subsequently, after it poured in methyl trimetoxysilane (MTMS) 20g on this liquid so that an interface might not be confused, and considering as the two-layer condition, the lower layer aqueous ammonia solution was gently agitated with the magnetic stirrer, and the hydrolysis reaction of MTMS was performed. When the upper MTMS disappeared, as a result of taking out a particle and observing a configuration by SEM, it had the projection with a height of 0.7-2.0 micrometers all over the particle, and was the konpeito-like particle whose last mean particle diameter is 5.8 micrometers. The SEM photograph Fig. of this particle is shown in drawing 2.

[0045] The same actuation as (1) - (3) in example 3 example 1 was performed, and seed fine particles were obtained.

(1) The 1l. glass flask was set to the constant temperature bath with a magnetic stirrer in which anomaly-ized processing temperature control is possible, the liquid which made this distribute the 10g of the

above-mentioned seed fine particles in 800ml of PVA water solutions 1% of the weight, and the liquid which mixed 0.1ml of aqueous ammonia 25% of the weight were put in, and temperature was held at 30 degrees C. Subsequently, after it poured in methyl trimetoxysilane (MTMS) 20g on this liquid so that an interface might not be confused, and considering as the two-layer condition, the lower layer aqueous ammonia solution was gently agitated with the magnetic stirrer, and the hydrolysis reaction of MTMS was performed. When the upper MTMS disappeared, as a result of taking out a particle and observing a configuration by SEM, it had the projection with a height of 0.2-1.1 micrometers all over the particle, and was the konpeito-like particle whose last mean particle diameter is 5.2 micrometers. The SEM photograph Fig. of this particle is shown in drawing 3.

[0046] The same actuation as (1) in example 4 example 1 and (2) was performed, and the 2nd seed particle liquid was prepared.

(1) Except that it set in the surface treatment example 1 (3), and Mn used PVA of 1000 for PVA of 500 instead of number average molecular weight (Mn), seed fine particles of the mean particle diameter of 4.2 micrometers and 1.9% of CV values were obtained like the example 1 (3).

(2) By the anomaly-ized processing example 1 (4), these conditions, and this approach, the hydrolysis reaction of MTMS was performed and the konpeito-like particle which has a projection all over a particle was obtained. This particle had the projection with a height of 0.2-0.6 micrometers all over the particle, and was a particle of the shape of konpeito whose last mean particle diameter is 4.9 micrometers.

[0047] In an example 5 and six examples 4, except that Mn used 3500 (example 5) and 70000 (example 6) instead of number average molecular weight (Mn) being PVA of 1000, it checked that a konpeito-like particle was obtained by the same actuation as an example 4.

[0048] In an example 7 and eight examples 4, except that Mn used the polyvinyl pyrrolidone (PVP) of 40,000 (example 7) and 1,200,000 (example 8) instead of number average molecular weight (Mn) being PVA of 1000, it checked that a konpeito-like particle was obtained by the same actuation as an example 4.

[0049] The same actuation as (1) in example 9 example 1 and (2) was performed, and the 2nd seed particle liquid was prepared.

(1) The 500ml glass beaker equipped with the surface-preparation churning motor and the impeller was set to the constant temperature bath, the 300ml of the above-mentioned 2nd seed particle liquid was added in the water solution adjusted [beaker / this] to 1% of the weight by polyoxyethylene-alkyl-aryl-ether [product made from the "noy gene EA-137 (HLB13)" first Heavy chemicals] 1.5g which is the Nonion system surface active agent, and 148.5g of ion exchange water, and churning mixing was carried out. Subsequently, after adding 15ml of aqueous ammonia 25% of the weight, it held and agitated for 12 hours and the surfactant adsorption PMSO particle (parent particle) of the mean particle diameter of 4.7 micrometers and 1.47% of CV values was obtained.

(2) By the anomaly-ized processing example 1 (4), these conditions, and this approach, the hydrolysis reaction of MTMS was performed and the konpeito-like particle which has a projection all over a particle was obtained. This particle had the projection with a height of 0.4-0.9 micrometers all over the particle, and was a konpeito-like particle whose last mean particle diameter is 5.8 micrometers.

[0050] In ten to example 15 example 9 instead of "noy gene EA-137 (HLB13)" "Noy gene EA-157 (HLB15)" (example 10) which is the Nonion system surfactant made from the first Heavy chemicals with which HLB differs from a class, "Noy gene EA-177 (HLB17)" (example 11), "noy gene EA-73 (HLB9)" (example 12), "Noy gene EA-143 (HLB14)" (example 13), "noy gene ES-149 (HLB14)" (example 14), It checked that a konpeito-like particle was obtained, respectively by the same actuation as an example 9 except having used "noy gene ET-147 (HLB14)" (example 15).

[0051] In example 16 example 9, it checked that a konpeito-like particle was obtained, respectively by the same actuation as an example 9 except having used "it is polyoxyethylene-alkyl-phenyl-ether "EMARUJITTO 9 (HLB 18-20) instead of noy gene EA-137(HLB13)" [the product made from the first Heavy chemicals]."

[0052] In example 17 example 9, it checked that a konpeito-like particle was obtained by the same

actuation as an example 9 instead of "noy gene EA-137 (HLB13)" except having used sodium dodecyl sulfate [SDS, HLB40, and the product made from the first Heavy chemicals].

[0053] In addition, for "noy gene EA-157" and "noy gene EA-177", as for polyoxyethylene dodecyl phenyl ether and "noy gene ES-149", polyoxyethylene alkyl aryl ether, "noy gene EA-73", and "noy gene EA-143" are [polyoxyethylene oleate and "noy gene ET-147"] polyoxyethylene alkyl ether.

[0054]

[Effect of the Invention] According to this invention, it crosses all over a parent particle and the silica system particle of the shape of konpeito which the projection of the shape of the shape of a ball or a semi-sphere bound firmly by the chemical bond mostly is obtained easily. This silica system particle can be suitably used for for example, the filler for resin, or a front face as a base material of the conductive particle which covered the conductive layer etc.

[Translation done.]